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PERFORMANCE EVALUATION OF FULL-SCALE HAZARDOUS WASTE INCINERATORS

VOLUME I

EXECUTIVE SUMMARY

by

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16. ABSTRACT

This report is Volume I, Executive Summary, of a series of extensive performance data EPA obtained through eight (8) field tests of actual industrial/commercial incinerators, was prepared in response to the Agency's need to conduct a regulatory impact analysis (RIA) for hazardous waste incinerators to determine the need, adequacy, and economic feasibility of current RCRA incinerator regulations. Tests involved trial burn-type testing at each plant during typical albeit closely monitored daily operations on wastes typical of their routine disposal function.

Most incinerators were found to be closely approaching or performing within RCRA requirements for destruction of compounds, although some facilities showed substandard results in other areas.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a five-volume series of reports presenting the recent testing and evaluation results of the performance of eight (8) commercial and industrial hazardous waste incinerators. The Agency's purpose was to gather accurate data on full-scale incinerator environmental performance, for the EPA's use in developing a regulatory impact analysis document in the near future for all such incinerators subject to existing RCRA standards. Because the performance information contained herein is of high interest to the hazardous waste incineration technical community in general, EPA wishes to make it available as a technical report at this time.

The material contained in this report has been reviewed and approved by experts within the Agency with state-of-the-art knowledge of the operation, testing, and evaluation of incinerator performance. During sampling and analysis of the incinerators in the field, EPA's most modern and scientific methods were employed along with the appropriate level of quality assurance and quality control. The incinerators were studied during a closely monitored mode of operation while disposing of mixtures of real-world hazardous wastes typical of their usual feedstocks. We are pleased to report that under these circumstances the incinerators were generally successful in performing their task of safely destroying hazardous waste and controlling other harmful emissions to the environment with some exceptions.

Requests for further information regarding this report on performance of full-scale incineration facilities should be directed to the Energy Pollution Control Division, IERL, Cincinnati.

David G. Stephan
Director
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ABSTRACT

This report describes a study to evaluate current baseline performance of hazardous waste incinerators. Tests were conducted at eight full scale facilities to characterize all feed and effluent streams. Pollutants measured included EPA Appendix VIII hazardous compounds, particulates, hydrogen chloride, carbon monoxide, and total hydrocarbons. The data were analyzed to address questions on Destruction and Removal Efficiency (DRE), products of incomplete combustion (PIC), pollutant emission levels, performance of air pollution control systems, and relationships of process parameters to destruction efficiency and emission levels. A large base of data on performance of hazardous waste incinerators was accumulated, and many possible relationtionships between parameters were explored. Conclusions included: DREs were generally above 99.99%; measured DREs tended to be higher when concentration of the hazardous compound in the waste was higher; the most frequently observed PICs were benzene, toluene, chloroform, tetrachloroethylene, and naphthalene; the particulate EPA regulation of 180 mg/Nm^3 was not routinely met; and the hydrogen chloride EPA regulation almost always met.

CONTENTS

Foreword iii
Abstract iv
Figures. vi
Tables vi
Acknowledgements vii

1.0 Introduction 1
2.0 Conclusions. 3
3.0 Program Description. 7
3.1 Summary of activities. 7
3.2 Overview of process characteristics. 9
4.0 Discussion of Results. 15
4.1 Organic emissions and their control. 15
4.2 HCl and particulate emissions and their control. 26
4.3 Quality of results 28
4.4 Sampling and analysis considerations 32

FIGURES

Number		Page
1	Waste characterization.	12
2	Penetration versus waste feed concentration - volatiles (fast VOST) - best available blank correction points. . .	17
3	Penetration versus waste feed concentration - semi-volatiles - blank corrected data.	19
4	Summary of average PIC concentrations	22
5	Percentage of PICs attributed to different mechanisms . . .	25

TABLES

Number		Page
1	Overview of Sampling and Analyses Activities.	8
2	Summary of Specific Data Evaluation Activities.	10
3	Distribution of Incinerator Types and Control Devices . . .	11
4	PICs Found in Stack Effluents	21
5	Ranges of Metals Emissions for Five Hazardous Waste Incinerator Tests	29

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The cooperation of all test sites and the efforts of many individuals in Midwest Research Institute's Environmental Systems and Analytical Chemistry Departments are also acknowledged.

SECTION 1.0

INTRODUCTION

The Environmental Protection Agency's (EPA's) Office of Solid Waste is conducting a Regulatory Impact Analysis (RIA) as part of EPA's hazardous waste incinerator regulatory development activities. The RIA includes definition of the baseline performance of incinerators operating under normal conditions and evaluation of the costs and benefits of alternative regulatory approaches. These analyses require knowledge of incinerator performance for different incinerator designs and operating conditions, a wide range of waste feed characteristics and various combinations of air pollution control equipment. This study of eight hazardous waste incinerators was conducted to provide input to the data base that will be used to characterize performance.

The overall goal of this study was to establish current baseline levels of performance through measurements of pollutant emissions (including over 40 Appendix VIII compounds) at the eight incinerators and to analyze the data generated from these measurements to identify performance trends. The primary measures of performance during this program were Destruction and Removal Efficiency (DRE) for Principal Organic Hazardous Constituents (POHCs) and removal of HCl and particulates from the stack gases, as described in the hazardous waste incinerator regulations (40 CFR 264, Subpart O, Sections 264.340-264.351). Specific topics that were addressed were: (a) baseline DREs that could be achieved by incinerators under "normal" operating conditions; (b) emissions of Products of Incomplete Combustion (PICs); (c) the impacts of incinerator operating conditions such as temperature, residence time, heat input, and excess air on DREs; (d) the impact of waste feed characteristics on DREs; (e) hydrogen chloride (HCl) and particulate emissions from incinerators with varied operating conditions and control systems; and (f) the effect of air pollution control systems on the emission of POHCs, HCl, and particulates.

Several caveats are needed to properly interpret the results of this study. First, this study was not intended to thoroughly document the relationships between incinerator designs and destruction of hazardous constituents. A rigorous experimental matrix of incineration parameters was not used nor were detailed facility characterizations prepared. Instead, the facilities were examined under normal operations with the fewest possible changes in typical operating conditions. As a result, the report does not provide a complete characterization of incinerator performance for specific POHCs under varied operating conditions. Second, the tests conducted were notofficial trial burns, although they did include all of the sampling and analysis normally required for trial burn testing. Third, new sampling and

analysis procedures were evaluated during the study. However, the study was not a methods development study, and the conclusions regarding sampling and analysis procedures should be interpreted accordingly.

The remainder of Volume I summarizes the results from the study in three sections. Section 2 presents the conclusions and recommendations. Section 3 defines the program approach and outlines major program activities. Section 4 presents the most significant results from the study.

More detailed information can be found in the complete program report (Volume II) and in the appendices (Volumes III, IV, and V). Volume III contains two appendices which document sampling and analysis activities. Volume IV contains the eight individual test reports in separate appendices. The internal and external Quality Assurance/Quality Control (QA/QC) appendices are contained in Volume V.

SECTION 2.0

CONCLUSIONS

A series of sampling and analysis activities for eight hazardous waste incinerators and subsequent data evaluation were used to greatly expand knowledge of hazardous waste incinerator performance. The activities also provided insight into potential problems and solutions to these problems as related to incinerator sampling and analysis. The conclusions related to incinerator performance as measured by organic emissions (DRE of POHCs and formation of PICs), particulate emissions and HCl emissions, the relationship of performance to continuous monitoring data; and sampling and analysis procedures are presented below.

1. Extensive analysis, discussed later in this volume, of organic emissions data provided the following insight into the factors affecting DRE:

- DREs for the incinerators tested were generally above 99.99%.
- DRE appears to be strongly correlated to concentration of the POHC in the waste feed. POHCs at higher waste feed concentrations were observed to be destroyed or removed to a higher degree. The phenomena that caused this relationship was not identified.
- Analyses of data collected on this program showed no clear correlation between DRE and heat of combustion for POHCs.
- Data compiled from the eight tests were not sufficient to define parametric relationships between residence time, temperature, heat input, or O_2 concentrations and DRE.
- The data from the eight tests suggest that POHC levels in scrubber water and ash were generally very low or nondetectable. These data suggest that the majority of POHCs are destroyed rather than merely transferred to another media in the incineration process.
- Some Appendix VIII compounds detected in the stack (primarily trihalomethanes) appear to be stripped from the scrubber water by the hot stack gas. Trihalomethanes detected in the scrubber inlet water were not detected in the effluent water. The effect can be lower measured/calculated DREs even though the destruction mechanisms may not be affected.

2. Evaluation of organic emissions data for compounds classified as Products of Incomplete Combustion (PICs are defined on this program as Appendix VIII compounds detected in the stack, which were not found in the waste feed in concentrations above 100 μg/g) led to the following observations:

- Stack gas concentrations of PICs were typically as high as or higher than those for POHC compounds in the stack.
- PIC output rate infrequently exceeded 0.01% of POHC input rate. (The 0.01% criteria was proposed in FR Vol. 45, No. 197, October 8, 1980.)
- The three likely mechanisms that explain the presence of most PICs are:
  a. Poor DREs for Appendix VIII compounds present at low concentration (< 100 μg/g) in the waste feed;
  b. Input of Appendix VIII compounds to the system from sources other than waste feed (e.g., scrubber water); and
  c. Actual intermediate products of combustion reactions or products of complex side reactions including recombination.
- Data from the tests suggest that benzene, toluene, chloroform, tetrachloroethylene, and naphthalene have a high potential for appearing as by-products of the combustion of organic wastes.

3. Compliance with the particulate standard of 180 mg/Nm^3 was not achieved at half of the sites tested. Particulate control devices were operated at five of the eight facilities, and two of these five failed to achieve the standard. Two of the three facilities without control devices also failed the particulate standard. Data from this study suggest that any facility firing wastes with ash content greater than 0.5% will need a particulate control device to meet the standard.

4. Carbon monoxide (CO) and total hydrocarbons (THC) were monitored on a continuous basis to assess their utility as indicators of incinerator performance. Analyses indicate that CO and THC may provide indication of changes in incinerator performance and gross malfunctions in the combustion process. However, under the conditions of these tests CO and THC levels did not appear to be good predictors of POHC emissions or DRE, either across plants or at a specific site, for DREs in the vicinity of 99.99%. It should also be pointed out that these tests were not conducted in a parametric fashion specifically designed to determine if such a correlation could be found.

5. HCl emissions were generally easily controlled to meet one of the two criteria specified in the regulations--less than 1.8 kg HCl/hr or greater than 99% removal efficiency.

6. Of the six sites that were tested for chlorinated dioxins and chlorinated furans, dioxins were found at one site and furans were found at three sites. No 2,3,7,8-TCDD was detected. The maximum concentrations detected were 0.06 ng/L of chlorinated furans and 0.02 ng/L of chlorinated dioxins.

7. A Volatile Organic Sampling Train (VOST) was developed and used during these tests. The VOST method provided a consistent and reliable data base when operated by personnel familiar with the apparatus and procedures. Proper use of these procedures was critical to obtaining reliable data.

8. Two methods were used on this program for sampling volatile organics in the stack--VOST and gas bags. When these two methods are compared, VOST provided better data on this program. The VOST method provided lower blank values than gas bags, resulting in a high percentage of quantifiable data points. The VOST method was less cumbersome and less prone to contamination than gas bags.

9. Hazardous waste samples contain a complex matrix of compounds which present a variety of analytical difficulties. Analysis by a gas chromatograph/mass spectrometer (GC/MS) was highly successful for identifying Appendix VIII compounds in the waste streams and effluents. Prescreening by a gas chromatograph/flame ionization detector (GC/FID) was useful when analyzing waste streams.

10. Because small concentrations of organics must be measured, sample contamination can present significant problems. Careful control of blanks and well defined blank correction procedures are required.

11. The results of the external and internal quality assurance program indicate that established quality assurance procedures were followed and the overall quality of laboratory and field work was adequate to meet the objectives of the study.

12. Evaluation of the QA/QC data for the eight incinerator tests indicated low or erratic recoveries in the analyses of phenol, cis- and trans-1,2-dichlorobutene, naphthalene, aniline, and bis(2-ethylhexyl)phthalate for the complex matrices encountered during this program. Caution should be used when evaluating these compounds as POHCs during actual trial burns. Further evaluation of analytical methods for these compounds is recommended.

13. The results from waste sampling and analysis at plants where Appendix VIII compounds were spiked into the liquid waste feed line indicate that inadequate mixing and, as a result, nonrepresentative samples may be a problem at some facilities. One approach to alleviate the problem is the use of in-line mixers. This approach was successful at the one facility where it was used during the program.

The conclusions presented above represent significant gains in the knowledge of incinerator performance and incinerator sampling and analysis. However, the data from the program were not sufficient to fully characterize incinerator performance, and the program was not intended to fully develop sampling and analysis methods.

SECTION 3.0

PROGRAM DESCRIPTION

This complex program encompassed a wide array of activities centered around testing at eight hazardous waste incinerator facilities. These activities included evaluation and, in some cases, modification of sampling and analysis methods; multimedia sampling and analysis, and extensive data evaluation to assess the performance of hazardous waste incinerators. This section provides a brief summary of the activities conducted during the program and an overview of important process characteristics at the eight sites tested.

3.1 SUMMARY OF ACTIVITIES

Initial review of sampling and analysis (S&A) methods needed to characterize sites and evaluate performance and consultation with EPA led to identification of the need for a better, more sensitive method to collect samples of volatile organic compounds in incinerator stack gases. A concept for a volatile organic sampling train (VOST) was developed at a meeting with EPA, and a laboratory study was planned to evaluate the concept. A short laboratory evaluation was then conducted using a simulated gas stream (see Appendix A).

Concurrent with the laboratory evaluation, general preparations were made to conduct a series of field tests, and QA/QC planning was conducted. As the eight sites were selected, site-specific test plans were developed. Sample locations, S&A procedures, and QA/QC planning were unique for each facility tested because of differences in system designs, operating practices, and waste characteristics. However, a similar overall approach was used.

The objective of the S&A activities was to characterize the performance of the eight incinerators with respect to organic, particulate, and HCl pollutants. Accomplishment of this objective required that each input and output stream be characterized to the greatest degree possible. Typical input streams included: waste feed, auxiliary fuel, and control system makeup and recyle waters. Output streams generally included: stack gases, control device effluent (solid or liquid), and incinerator bottom ash. Each stream sampled was generally analyzed for organic constituents, chlorides, particulate or ash, and in some cases, metals. An overview of the sampling and analysis activities that spans the total program is presented in Table 1. Detailed descriptions of the activities for each site are presented in Volume IV (Appendices C-J). Descriptions of the S&A methods and procedures are presented in Volume III (Appendix B).

TABLE 1. OVERVIEW OF SAMPLING AND ANALYSES ACTIVITIES[a]

Stream	Sampling method/technique	Analyses
Liquid feed	Grab	HHV POHC Cl^- H_2O Ash Metals Viscosity
Solid feed	Grab	HHV POHC Cl^- H_2O Ash Metals
Control device makeup water	Grab	Chloroform Cl^- POHCs pH
Control device effluent	Grab	pH POHC Cl^- Metals
Ash	Grab	POHC Cl^- Metals EP toxicity
Stack	MM5	Particulate Metals Semivolatile POHC Semivolatile PIC Cl^-
	VOST	Volatile POHC Volatile PIC
	Gas bag	Volatile POHC Volatile PIC
	Gas bag	Orsat CO_2 O_2
	Continuous monitors	CO CO_2 O_2 THC

[a] Not all sampling and analysis activities listed were conducted at each facility.

The S&A activities generated a very large number of data points of potential use to evaluate incinerator performance. The objectives of the data evaluation phase of the study were: (a) to reduce the data to a format that is more useful for evaluating incinerator performance; (b) to define those incinerator and waste parameters that have the greatest impact on incinerator performance; (c) to evaluate the magnitude of those impacts to the degree possible within the available data base; and (d) to assess the overall quality of the data generated during a trial burn. To accomplish these objectives the data evaluation was divided into three distinct activities: (a) data reduction and calculations; (b) specific issue analyses; and (c) pattern recognition activities.

The initial data evaluation activity was the development of procedures to reduce data to a format most useable for subsequent analyses. Activities under this segment included evaluating and defining procedures for calculating chloride and POHC input rates, blank correction procedures for POHC effluent rates, and calculation of the most representative residence time and excess air for each of the eight facilities.

A number of specific technical issues related to incinerator performance were identified throughout the program. Specific engineering and statistical analysis techniques appropriate to each problem were selected and, to the degree possible within the available data base, conclusions were drawn. Table 2 identifies the major specific issues addressed during the program and the analytical techniques used.

The objective of the pattern recognition component of the data evaluation effort was to identify relationships between parameters that were not apparent from the overall examination of the data. To achieve this objective, the pattern recognition approach employs a variety of multivariate statistical techniques. The two techniques that were most productive on this program were factor analyses, which identified the parameters that contributed most significantly to the overall variation in the test data, and discriminant analyses, which were used to identify the incinerator and waste characteristics that contributed most significantly to the achievement or nonachievement of 99.99% DRE.

3.2 OVERVIEW OF PROCESS CHARACTERISTICS

The eight hazardous waste incinerators tested during this study were selected by EPA to provide a broad representation of the incinerators in the country. These eight incinerators span a wide array of incinerator design and operating parameters, particulate and HCl control equipment, and waste feed characteristics. Some of the more important characteristics include incinerator type such as liquid injection, rotary kiln, and hearth; incinerator operating parameters such as combustion temperature, residence time, heat input rate, and the excess air; type and operating characteristics of particulate and HCl control equipment; and waste characteristics such as physical state, organic content, moisture content, heating value, and ash and chloride content.

TABLE 2. SUMMARY OF SPECIFIC DATA EVALUATION ACTIVITIES

Issues	Analytical Techniques
Assessment of overall data quality	Multiple techniques including calculation of descriptive statistics related to accuracy and precision, and chemical and engineering analyses of potential problems and causes
Relationship beteen DRE and heats of combustion	Nonparametric rank order correlation
Relationship between DRE and waste feed concentration	Linear regression on log transforms and Engineering analysis of potential reaction rates
PIC formation	Chemical and engineering analyses of potential formation mechanisms Graphical comparison of PICs and POHCs
Potential for Dioxin/Furan formation	Review of Dioxin/Furan formation and presence of precursors in waste
Relationship of CO/THC concentrations to POHC stack concentration and DRE	Nonparametric statistics - rank order correlation and distribution free rank sum test
Performance of air pollution control equipment	Comparison of data between systems and engineering analysis of system performance
Achievability of 99.99% DRE	Multiple techniques including comparison of basic descriptive statistics, linear regression analyses, and discriminant analyses

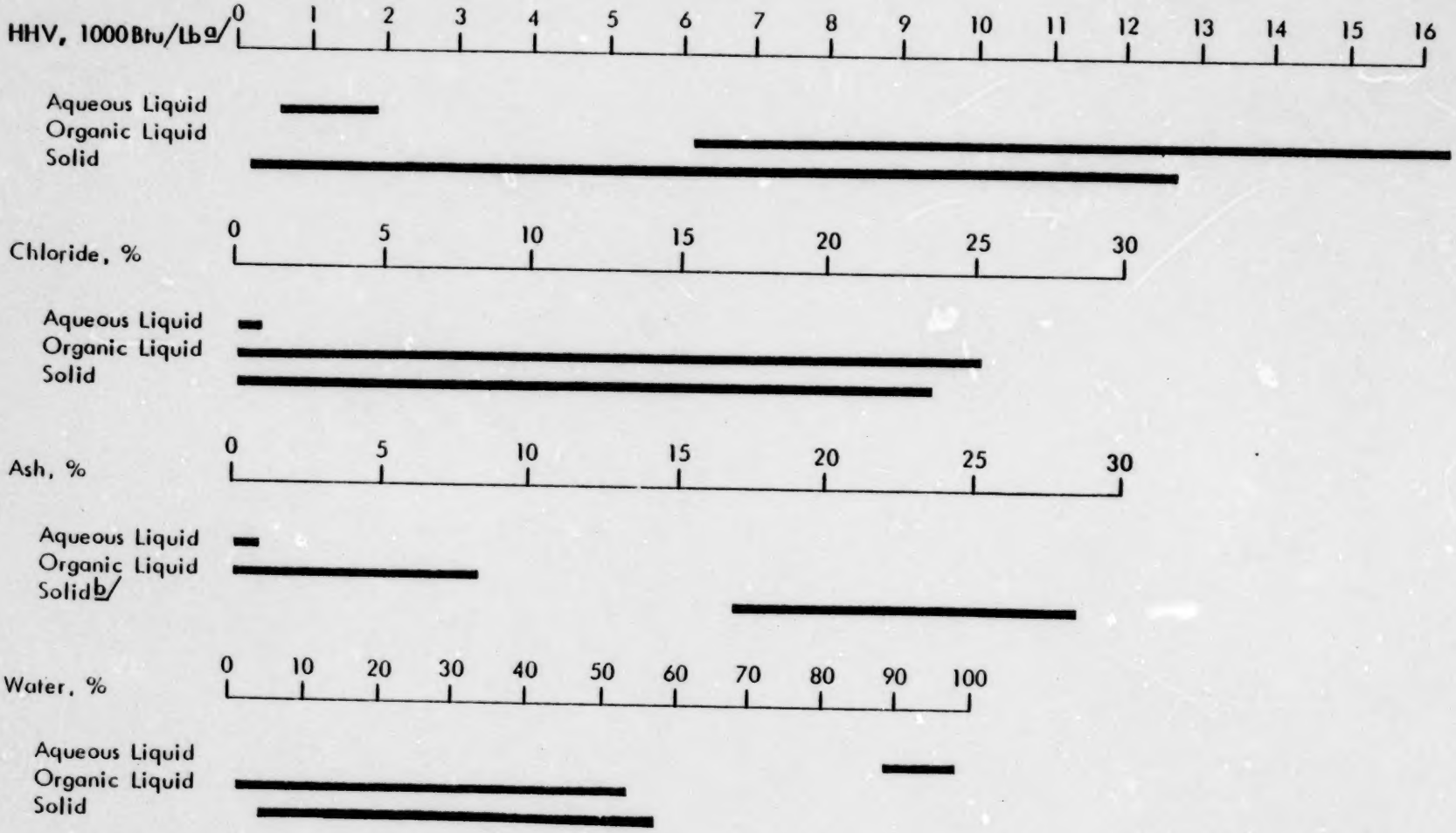
The distribution of incinerator types and control devices is shown in Table 3. Each of the eight incinerators had liquid injection burners; four of those fired both organic and aqueous wastes during the tests. Three of the facilities fired solid wastes (two rotary kilns and one hearth) and one ducted gaseous waste to the incinerator during testing. Three incinerators had no air pollution control devices, and the other five had scrubbers for HCl control. Particulate control devices were used at four plants.

TABLE 3. DISTRIBUTION OF INCINERATOR TYPES AND CONTROL DEVICES

Incinerator type	Number of facilities
Liquid injection	8
Rotary kiln	2
Hearth	2
Gas injection	1
Control device	**Number of facilities**
None	3
HCl scrubber	5
Particulate control	4

The facilities exhibited a wide range in capacity of 1 to 78 GJ/hr (1 to 74 million Btu/hr) heat input. Values for three key parameters: combustion temperature, residence time, and percent excess air or percent oxygen also varied widely. Operating temperatures ranged from 650° to 1450°C and calculated residence time varied from 0.07 to 6.5 sec. Excess air values fell within a range of 60 to 130%. Corresponding oxygen content ranged from 8 to 12%.

Waste feeds with a wide range of characteristics were encountered at the eight sites. Figure 1 shows the variation in some waste characteristics by type of waste. The heating values were below 4,600 kJ/kg (2,000 Btu/lb) for aqueous liquids and ranged from 14,000 to 37,000 kJ/kg (6,000 to 16,000 Btu/lb) for organic liquids, and from 0 to 29,000 kJ/kg (0 to 12,500 Btu/lb) for solid wastes. The organic liquids and many of the solids had a high enough heating value to sustain combustion without auxiliary fuel. Percent chloride in the wastes ranged up to 25%, with the highest values occurring for organic liquids (chlorinated solvents). Little ash was found in aqueous liquids, values for organic liquids ranged up to 9%, and solids had the most ash with values from 17% to 29%. Water content is obviously high for the aqueous wastes, but ranged up to 50 to 60% for the organic liquids and solids.



a/ 1,000 Btu/Lb = 2,300 kJ/kg
b/ Does not include sand spiked with chlordane at TWI

Figure 1. Waste characterization.

Operating conditions during the tests were those selected by the plants as their normal conditions. In general, any existing operating problems were corrected before the tests were initiated.

SECTION 4.0

DISCUSSION OF RESULTS

Two key questions that provided the overall focus for this program were: (a) how well can hazardous waste incinerators typically perform, and (b) what conclusions about, or insights into, the performance of an incinerator can be drawn from other trial burn results? Complex issues involving sampling and analysis procedures, incinerator design and operating characteristics, and control equipment design and performance affect the answers to these questions. While the results of this program do not provide complete answers to the two questions, they do provide information that will contribute to understanding a number of related specific issues.

This section presents the more significant results that provide insights to those two questions. These results are broken into four subsections--organic emissions and their control; HCl and particulate emissions and emissions control; quality of results; and sampling and analysis considerations. The results presented in those subsections are discrete pieces of information related to incinerator performance and testing of that performance, rather than a cohesive body of knowledge that fully characterizes incinerator performance. A more detailed discussion of results is in Volume II.

4.1 ORGANIC EMISSIONS AND THEIR CONTROL

Two primary measures of incinerator performance are DREs for POHCs in the waste feed and emission rates for PICs. This section examines key results related to those two measures. In the paragraphs below an overview of DRE measurements is presented, and relationships between DRE and incinerator and waste feed characteristics are discussed. An overview of PIC emissions and an analysis of possible mechanisms that may explain the presence of these PICs are also presented. Finally, relationships between continuous measurements for carbon monoxide (CO) and total hydrocarbons (THC) and concentrations of hazardous organic compounds in the stack gas are examined.

4.1.1 POHCs

One key element of this study was determination of DREs for any POHC present at 100 ppm (approximate detection limit) or greater in any waste feed stream. The DREs span a wide range for both volatile and semivolatile compounds. The 134 volatile and 106 semivolatile data points (a data point is one test run for one compound) are distributed as follows:

Type of POHC	DRE Range				
	< 99	99-99.9	99.9-99.99	99.99-99.999	> 99.999
Volatiles	2	12	30	51	39
Semivolatiles	3	5	20	46	32

DREs < 99.99% tend to occur when one or both of two factors are present. The first factor is low concentration of the POHC in the waste feed (i.e., < 1,000 μg/g). The second factor involves compounds commonly identified as PICs (esp. chloroform, methylene chloride, benzene, and naphthalene). The formation of these compounds during the incineration of chlorinated organics increases their concentration in the stack gas, resulting in a lower DRE. Eighty percent of the volatile points and 96% of the semivolatile points below 99.99% DRE occurred in cases where one or both of these factors were present.

Some observations from the data base are: (1) the eight facilities achieved an average DRE of 99.992% for all volatile compounds; (2) although an average for semivolatile compounds cannot be calculated because over half the stack measurements were below detection limits, the only semivolatile compounds measured which did not consistently achieve at least 99.99% DRE were phenol, bis (2-ethylhexyl)phthalate, diethyl phthalate, naphthalene and m-dichlorobenzene; and (3) only two of the eight sites achieved an average DRE of 99.99% for every semivolatile and volatile POHC.

As a part of efforts to predict incinerator performance, a variety of relationships between DRE and waste feed and incinerator operating parameters have been postulated. The data analysis portion of the program addressed three types of relationships--the effect of waste feed concentration on DRE; the relationship between DRE and heats of combustion for specific POHC, and the impact on DRE of such incinerator parameters as temperature, residence time, and stack O_2 concentration. The results of these analyses which, because of the number of facilities tested and the variety of designs and conditons at each, cannot be considered definitive are summarized below.

The relationship between DRE and waste feed concentration was examined using linear regression analyses. Separate regression analyses were conducted for volatile and semivolatile compounds using the log transforms for both penetration (1-DRE) and waste feed concentration.

For volatile compounds, the data were best fit by a line with a slope of -0.79. Figure 2 shows no compounds below 200 μg/g in the waste feed achieved a DRE greater than 99.99%. Only one compound below 1,000 μg/g in the waste feed achieved a DRE greater than 99.99%. Only three points above 10,000 μg/g did not achieve a DRE greater than 99.99%, and no points above 12,000 μg/g failed to achieve 99.99% DRE. The correlation coefficient of -0.84 for the regression line is highly significant.

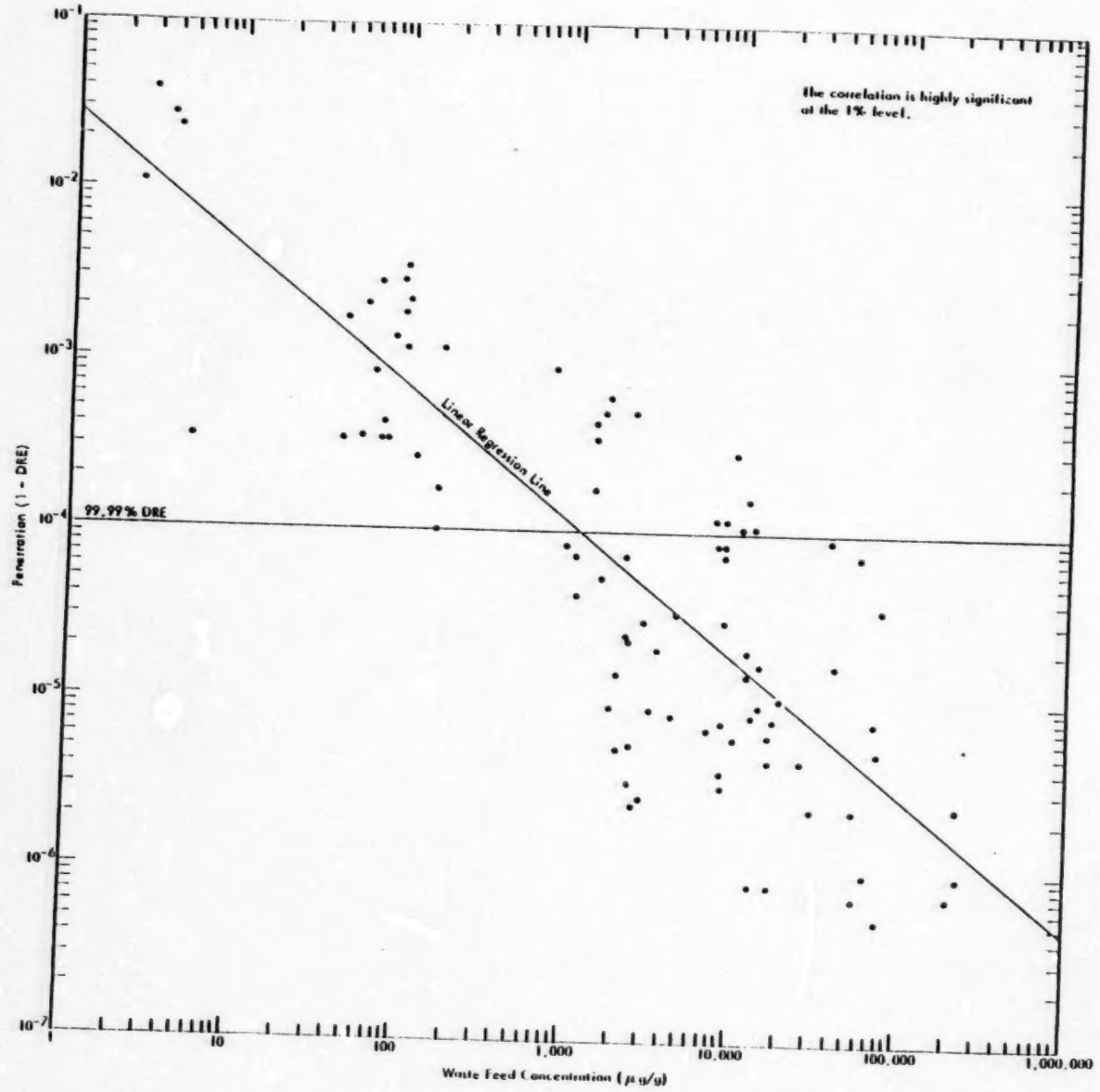


Figure 2. Penetration versus waste feed concentration - volatiles (fast VOST) - best available blank correction points.

A similar comparison using the data for semivolatile POHCs showed the same basic relationship (see Figure 3). The slope of -0.81 is comparable to that obtained for volatile compounds. A statistically significant correlation coefficient of -0.76 was obtained.

To further investigate the trend established above, the data were analyzed from two additional points of view. First, the data base was expanded to include all points in order to determine if the blank correction process biased the data base by eliminating points which fell near the detection limit. Second, the range of waste feed concentrations represented by this trend was extended by examining waste feed analyses for compounds which might have been present in feed streams at low concentrations (< 100 μg/g). For three of the facilities, waste feed concentrations down to 1 μg/g were measured for some of the waste feed streams. Both of these analyses confirmed the trend.

Both plant specific and compound specific analyses were also conducted. Each of these analyses produced the same general trend of increasing DRE with waste feed concentration.

The relationship between DRE and the heat of combustion of a POHC was examined statistically. The analysis was based on data from the four facilities which had sufficient quantifiable points to provide a meaningful analysis. If the incinerability of a compound were dependent on its heat of combustion, the DREs for compounds subject to the same incinerator conditions should be positively correlated with the heats of combustion of those compounds. None of the data for the four plants show a significant positive correlation, and data from two of the four show a significant negative correlation between DRE and heats of combustion.

Multivariate statistical analyses were used to examine the impact of four incinerator operating parameters--residence time, chamber temperature, heat input rate, and stack O_2 concentration--on DRE. Because the analyses were restricted by a limited number of data points and were taken from sites that were not selected randomly from the population, the data should be interpreted with caution. The results indicate relationships which warrant further investigation; they do not establish definitive relationships between the operating parameters and DRE.

The results of two types of multivariate analyses, factor analysis and discriminant analysis, indicate that the only operating variable strongly related to DRE is chamber temperature. However, the data were not sufficient to define a quantitative relationship between temperature and DRE. The results suggest that, for the sites tested, factors such as waste feed concentration, specific compound kinetics, and PIC formation tend to mask relationships between incinerator operating conditions and DRE.

Measured DREs may also be affected by scrubbers. Scrubbers can act to increase or decrease measured DREs, respectively, by: (a) removing POHCs from the gas stream by absorption; or (b) adding POHCs to the gas stream by stripping from the scrubber influent. Each of these mechanisms is discussed briefly below.

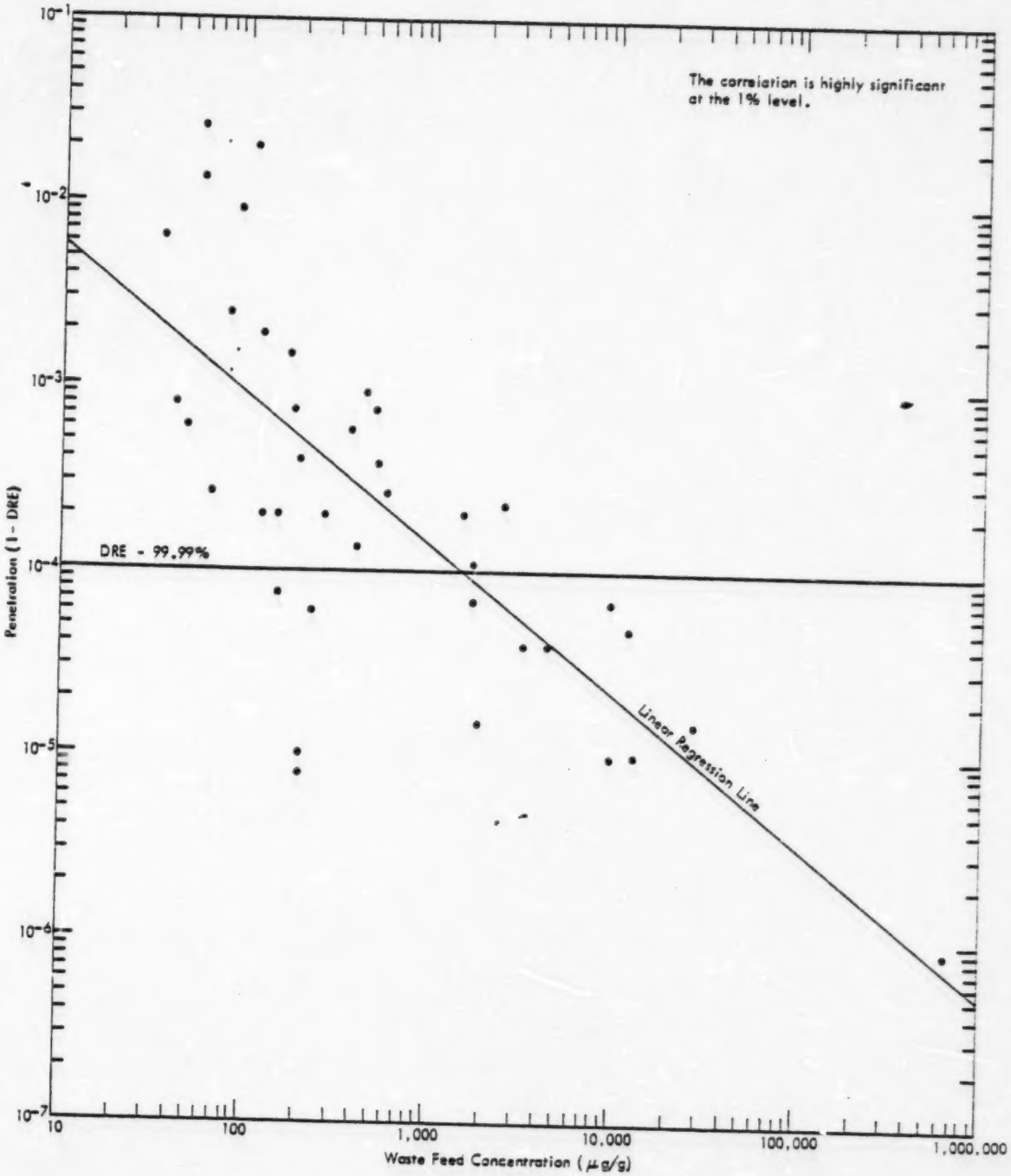


Figure 3. Penetration versus waste feed concentration - semivolatiles - blank corrected data.

Effluent scrubber waters were analyzed for POHCs at five facilities which had wet scrubbers to determine if organics were removed from the gas stream. At one plant naphthalene was detected at 35 µg/L in the scrubber effluent. Otherwise toluene, phenol, and naphthalene were present in effluents at several sites at concentrations less than 20 µg/L. These low levels suggest that scrubbers generally do not remove significant quantities of POHCs from the stack gas.

In several cases, the control system added to the concentration of POHCs in the stack gas. The scrubber influent at three facilities contained about 100 µg/L of chloroform, while the effluent contained no measurable amounts. In all three cases, the quantity of chloroform lost from scrubber waters accounts for all chloroform detected in the stack. Scrubber waters also appear to contribute small quantities of other trihalomethanes to stack gases.

4.1.2 PICs

A second consideration related to the incinerator performance is the formation of PICs in the combustion chamber. As indicated earlier, a PIC is any Appendix VIII organic hazardous constituent that is not present in the waste feed at concentrations greater than 100 ppm.

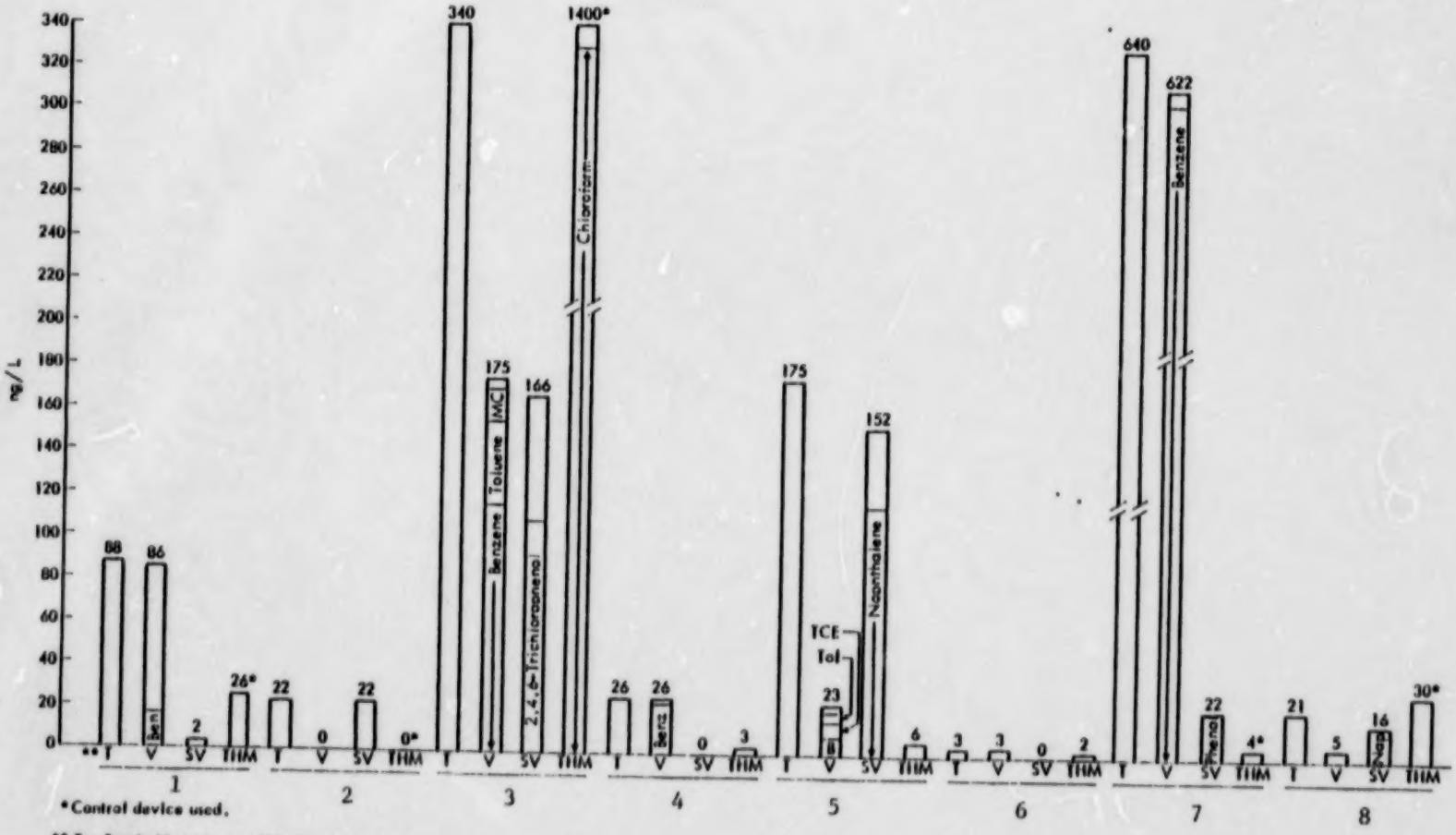
As a part of this study, stack gas samples were analyzed for PICs, and possible mechanisms of PIC formation were examined. This section presents the results of those analyses. Basic data on PIC emissions are presented, and PIC emission rates are compared to POHC emission rates. Three possible mechanisms that explain the presence of PICs and the potential contributions of these mechanisms are described. Finally, data are presented on two families of PICs that are of particular interest--dioxins and furans.

Approximately 30 compounds were classified as PICs from the eight tests (see Table 4). They were detected over a wide range of stack gas concentrations. Compounds present in most or all of the stacks, either as POHCs or PICs, are the hazardous organics which are most likely to be actual products of the incomplete combustion of hazardous constituents.

The concentrations of PICs at the eight different facilities are presented in Figure 4. The PICs are divided into three categories: volatiles; semivolatiles, and trihalomethanes (THM's: chloroform, bromodichloromethane, dibromochloromethane, and bromoform). Trihalomethanes are not included in the totals due to the possibility that they may be contributed by the scrubbing systems at some facilities. Total PIC levels were also compared to total POHC levels for the eight facilities. On the average, the PIC levels were slightly higher than the POHC levels, although this relationship varies widely from facility to facility. Calculations were carried out to determine PIC output rates as a percentage of the POHC input rates. At only one of the eight tests were PIC output rates greater than 0.01% of POHC input rates.

TABLE 4. PICs FOUND IN STACK EFFLUENTS

PIC	Number of sites	Concentrations (ng/L)
Benzene	6	12-670
Chloroform	5	1-1,330
Bromodichloromethane	4	3-32
Dibromochloromethane	4	1-12
Bromoform	3	0.2-24
Naphthalene	3	5-100
Chlorobenzene	3	1-10
Tetrachloroethylene	3	0.1-2.5
1,1,1-Trichloroethane	3	0.1-1.5
Hexachlorobenzene	2	0.5-7
Methylene chloride	2	2-27
o-Nitrophenol	2	25-50
Phenol	2	4-22
Toluene	2	2-75
Bromochloromethane	1	14
Carbon disulfide	1	32
Methylene bromide	1	18
2,4,6-Trichlorophenol	1	110
Bromomethane	1	1
Chloromethane	1	3
Pyrene	1	1
Fluoranthene	1	1
Dichlorobenzene	1	2-4
Trichlorobenzene	1	7
Methyl ethyl ketone	1	3
Diethyl phthalate	1	7
o-Chlorophenol	1	2-22
Pentachlorophenol	1	6
2,4 Dimethyl phenol	1	1-21



*Control device used.

** T = Total, V = Volatile SV = Semivolatile
THM = Trihalomethanes - chloroform, bromoform, bromodichloromethane, dibromochloromethane (not included in other totals).

Figure 4. Summary of average PIC concentrations.

Three suggested explanations for the presence of PIC compounds are: (a) the compounds were actually present at low concentrations (< 100 μg/g) in the feed and were destroyed at a relatively low DRE; (b) the compounds were introduced to the system from some source other than the waste; and (c) the compounds are formed as products of combustion reactions.

The estimated stack concentration for a compound present in the waste feed just below the POHC limit of 100 μg/g and subject to a DRE of 99.9% is 10 ng/L. As explained in Section 4.1.1, this low DRE becomes very plausible when the trend of DRE versus concentration in waste feed is examined. The trend of decreasing DREs shows that many of the PICs detected could be explained by low concentrations in the feed.

Other potential sources of organic constituents in the stack gas are feed waters to pollution control systems, inleak air and auxilliary fuel. The discussion in Section 4.1.1 provided evidence of the potential contribution of makeup waters to PIC emissions, particularly trihalomethanes. Inleakage of air downstream from the combustion chamber may contribute to PIC emissions. Analysis of data from one facility where ambient concentrations of organic constituents were available and estimates of inleak air could be developed, indicated that inleak air could account for up to 10% of some organic constituents detected in the stack. Finally, analysis of auxilliary fuel oil at one plant indicated that this source could be a major contributor for some POHCs. If fuel oil streams are not analyzed, they could contain Appendix VIII compounds that are not present in the waste feeds. Those constituents which were subsequently detected in the stack would be classified as PICs.

The third mechanism, the actual formation of combustion reaction products, is the least understood of the three possibilities. The occurrence of simple stable compounds such as chlorinated methanes, ethanes, and benzene compounds in most stacks supports the hypothesis that PICs may be formed during combustion reactions. Primary candidates for this list on the basis of these tests include compounds which were present in all stack samples regardless of their presence in the waste feed: methylene chloride; chloroform; carbon tetrachloride; trichloroethylene; tetrachloroethylene; 1,1,1-trichloroethane; benzene; toluene; chlorobenzene; naphthalene; and phenol. Either benzene or toluene accounted for the highest measured stack concentrations of any compound at seven of the eight tests. This occurred regardless of whether the compounds were listed as a POHC or PIC.

To prove the hypothesis that certain compounds are formed as PICs would require analyzing the numerous reactions which could occur with complex mixtures of waste feeds on a plant by plant basis. In addition to differences in waste feed compositions, certain incinerators may have uneven temperature distributions, poor mixing conditions, or low temperature areas which might lead to poor combustion conditions, resulting in an increased likelihood for the formation of PICs. All of these factors would have to be taken into account in the determination of specific mechanisms for the formation of common products of incomplete combustion. Such analyses are beyond the scope of this program.

Figure 5 summarizes the relative potential contribution of each of these mechanisms to the total mass output of PICs. Low concentration POHCs in the waste feed potentially accounted for 0 to 68% of the total mass of PICs detected at each facility. The higher percentages were for the plants with the lowest total mass of PICs. The stripping of trihalomethanes from the waters potentially accounted for up to 14% of the total mass of PICs detected. The rest of the compounds were most likely actual products of combustion reactions.

Figure 5 also includes a bar which represents the percent of the PICs which fall into the following list of most common compounds (MC) based on frequency of occurrence and concentration:

Compound	Concentration Range (μg/L)	Number of Plants as a PIC
Chloroform	1.5 - 1,330	5
Benzene	13 - 670	6
Naphthalene	4 - 120	3
o-Nitrophenol	25 - 35	2
Bromoform	0.21 - 23	3
Phenol	5 - 19	2

This brief list accounts for a substantial percentage of total PIC output at half of the facilities.

Stack emissions at six of the eight facilities were analyzed for tetrachlorodibenzofurans (TCDF), pentachlorodibenzofurans (PCDF), tetrachlorodibenzodioxins (TCDD), and pentachlorodibenzodioxins (PCDD). Furans were detected at three facilities and dioxins at only one. Detection limits ranged from 0.0003 to 0.002 ng/L. Concentration ranges were:

TDCF:	0.0007-0.047 ng/L
PCDF:	0.0005-0.023 ng/L
TCDD:	0.021 ng/L
PCDD:	0.001 ng/L

Three TCDD isomers were identified 1,2,6,8-TCDD; 1,2,3,6- or 1,2,7,8-TCDD; and 1,3,6,8- or 1,2,4,7- or 1,2,4,8-TCDD. No 2,3,7,8-TCDD was detected.

4.1.3 Comparison of CO and THC Concentrations to Organic Emissions

CO and THC were monitored continuously during the testing at each of the eight sites. These data were subsequently reduced and compared to both POHC concentrations and DRE using statistical techniques. The results generally indicated that continuous monitors for THC and CO may provide some indication of incinerator performance but that they are not good predictors of POHC concentrations either at specific plants or across plants. In particular the results showed that CO is positively correlated with POHC

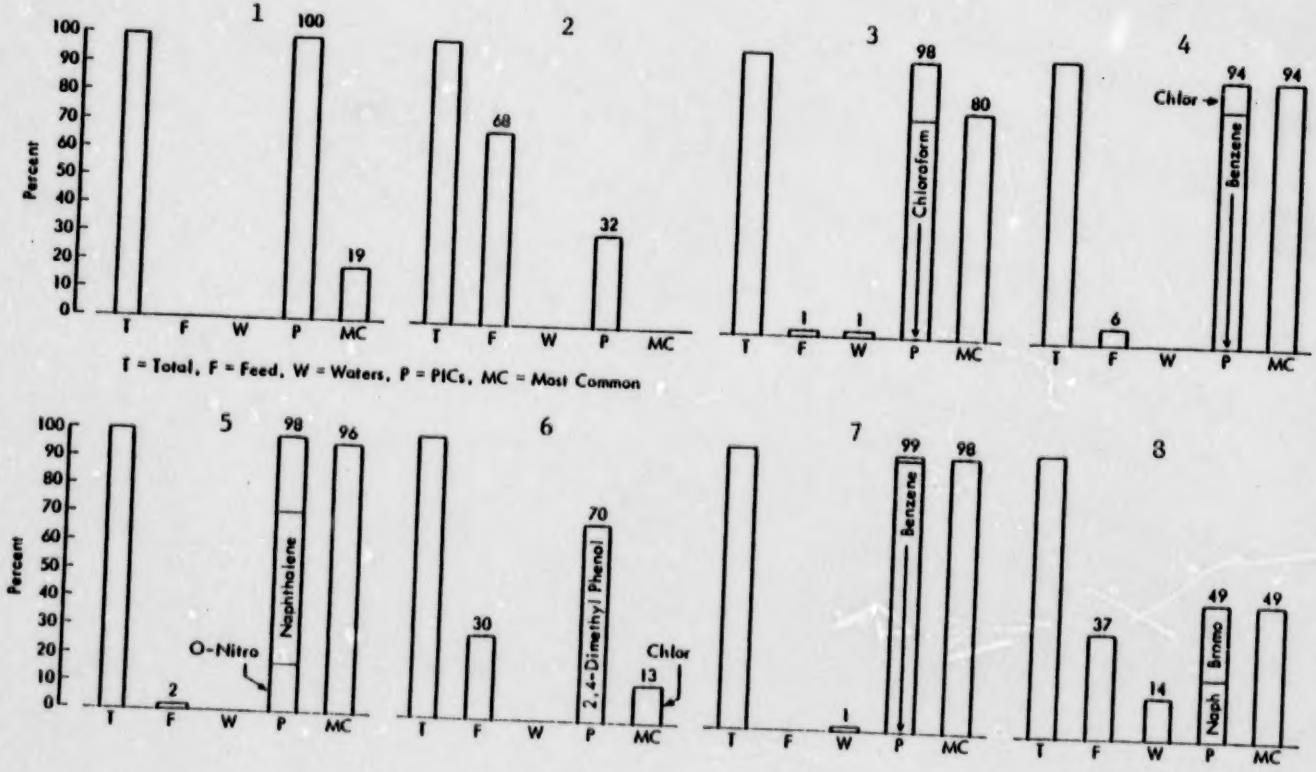


Figure 5. Percentage of PICs attributed to different mechanisms.

concentrations when CO concentrations are above 50 ppm, but high POHC concentrations are also measured when CO concentrations are below 50 ppm. For THC concentrations of POHCs are measurably higher when THC concentrations are above 10 ppm than when they are below 10 ppm. However, no correlations between THC concentrations and POHC concentrations were exhibited when THC concentrations were above 10 ppm.

Nonparametric methods were also used to compare CO concentrations to DRE. The analysis compared the average CO concentration for a run to the penetration (1-DRE) of a specific POHC for the same run using the data for carbon tetrachloride, toluene, trichloroethylene, and tetrachloroethylene. The concentrations of CO and penetration were not positively correlated for any of the four compounds.

These results from the nonparametric analyses were confirmed by parametric multivariate analyses. Principal component analysis was conducted with data from the last five tests for six compounds - benzene, toluene, trichloroethylene, carbon tetrachloride, methylene chloride, and tetrachloroethylene. The objective of the principal component analysis is to identify the key variables that had the greatest impact on the variation among the test observations. As an intermediate product, the method produces correlation coefficients for all input variable pairs. This matrix showed no correlation between CO or THC and stack concentration of organic constituents or DRE.

4.2 HCl AND PARTICULATE EMISSIONS AND THEIR CONTROL

Although the major concerns related to hazardous waste incinerator emissions have focused on organic constituents in the exhaust gases (i.e., DRE), chloride emissions and particulate emissions (including metals emissions), are also of concern. These emissions are covered by current hazardous waste incinerator regulations. HCl emissions are limited to the greater of 1.8 kg/hr (4 lb/hr) of HCl or 1% of the total organic chloride in the waste. The maximum allowable particulate concentration is 180 mg/Nm^3 (0.08 gr/dscf) as corrected to 7% O_2.

Add-on air pollution control devices are frequently used to achieve compliance with the regulations, because control of HCl and particulate emissions is not inherent to combustion. One of the objectives of the study was to evaluate the performance of these HCl and particulate control systems. The degree to which this objective could be addressed was limited by the constraints placed on sampling activities by the facility designs. Only one of the eight facilities had a control device inlet sampling location suitable for testing. As a result, only limited analyses of performance based on outlet sampling could be performed.

The available information on HCl and particulate emissions and emissions control is briefly summarized below. A description of the control systems, discussions of HCl and particulate emissions, and a synopsis of available metals data are presented. Because of the paucity of data upstream from control systems the discussion is primarily a presentation of available data rather than an analysis of performance.

Essentially all hazardous waste incinerators that require add-on HCl control equipment use some type of countercurrent wet scrubber for HCl removal. Since HCl is highly soluble in water an aqueous scrubbing liquid, sometimes containing caustic for pH control, is generally used. Five of the eight facilities used wet scrubbers for HCl control. Three of the systems had single-stage systems while two had multistage systems. Two of the systems used water only as a scrubbing media; the other three added caustic for pH control. While the systems did vary significantly, all five appear to be within normal ranges with respect to key design parameters.

All eight facilities tested performed well with respect to the HCl emissions regulations. Two of the three facilities with no control had little chloride in the waste and easily complied with the mass emissions standard of 1.8 kg/hr. At the other facility almost all the chlorides in the waste feed were the result of spiked carbon tetrachloride and trichloroethylene. Under normal operating conditions this facility almost certainly would have complied with the standard.

The five facilities with HCl control complied with the standard with the exception of a single run at one facility. Three of the facilities with packed towers achieved greater than 99% HCl removal and emitted less than 1 kg/hr on all runs. One of the facilities which had only a venturi scrubber with mist eliminator consistently achieved 97 to 98% HCl removal and emitted less than 0.3 kg/hr of HCl. The one facility which failed to achieve the standard had a single packed bed scrubber. This facility achieved about 99% HCl removal efficiency and emitted less than 1 kg/hr of HCl on two runs. On the third run, the removal efficiency was 96% and the HCl emission rate was 2.0 kg/hr. No reason for the decreased performance on the third run was identified.

A variety of control techniques have been used to control particulate emissions from hazardous waste incinerators. The most common techniques include venturi scrubbers and ionizing wet scrubbers. Five of the eight facilities tested during this program had some type of particulate control. Two had high energy wet scrubbers, one had a low energy wet scrubber (which provides minimal control), one had an ionizing wet scrubber, and one had an electrified gravel bed filter, a novel control device.

The data collected during this study indicate that achieving the particulate emissions limitation of 180 mg/Nm^3 (corrected to 7% O_2) may be more difficult than achieving either the HCl or DRE standards for hazardous waste incinerators. This conclusion holds true for incinerators with and without particulate control devices. The data that form the basis for this conclusion are summarized below.

The data from three facilities with no particulate control device suggest that any facility firing wastes with ash content greater than 0.5% will clearly have difficulty achieving the particulate limit without add-on particulate controls. At ash contents of 0.2 to 0.5%, facilities may still have difficulty meeting the limit without controls. Each of these three facilities fired liquid organic wastes. One facility with extremely low ash (0.1% or less) easily complied with the standard. A second facility

with wide ranges in ash content (< 0.005% to 0.5%) had mixed results. At < 0.05% ash emissions easily complied with the limit; at 0.2% ash, emissions marginally complied with the limit; and at 0.5%, ash emissions exceeded the limit by a factor of 2. The third facility had ash contents ranging from 0.7 to 0.8%. Emissions from this facility exceeded the 180 mg/Nm^3 limit by factors of 4 to 6.

Two of the five facilities with particulate control systems failed to comply with the emission limit and two achieved marginal compliance. The one facility with a venturi scrubber with an extremely high pressure drop (~ 30 kPa or 100 in H_2O) easily complied with the limit. The results for four systems are summarized below:

Control Type	Stack Particulate Concentration (mg/Nm^3)	
	Range	Average
Venturi Scrubber	10.4-33.7	23.0
Ionizing Wet Scrubber	139-176	151
Venturi Scrubber	102-290	169
Packed Bed Scrubber	183-217	200

In summary, average outlet concentrations for the eight facilities tested (controlled and uncontrolled) ranged from 23 to 900 mg/Nm^3. Four of the eight facilities failed to meet the limit of 180 mg/Nm^3 and two additional facilities complied with the limit by a margin of less than 20%.

Metals contained in the waste feed to incinerators eventually emit from the incinerator by one of three pathways--as part of the particulate emissions (or vapor) from the stack, in liquid or solid effluents from the control device, or in the incinerator ash. Metals were analyzed in selected samples of these effluent streams from five of the eight facilities tested during this program. The analysis focused on the 12 metals identified in Appendix VIII as hazardous constituents--antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, and thallium.

The data from these analyses were not sufficient to complete an overall materials balance for metals. A summary of the air emissions data for the five tests is presented in Table 5. Evaluation of other metals pathways are discussed in Volume II.

4.3 QUALITY OF RESULTS

Extensive resources were allocated on this program to assess the quality of results because: (a) those results affect the conclusions drawn from this program about overall incinerator performance; and (b) additional information about the quality of results from trial burn type tests will assist in evaluating results from future trial burns. The assessment of the quality

TABLE 5. RANGES OF METALS EMISSIONS FOR FIVE HAZARDOUS WASTE INCINERATOR TESTS

Metals	Emission range	
	µg/g of Particulate	g/min
Antimony	< 1,200 - 15,200	< 0.012 - 1.2
Arsenic	ND[a]	ND[a]
Barium	41 - 3,090	0.0032 - 0.12
Beryllium	< 0.32 - 6	< 0.0001 - 0.002
Cadmium	140 - 4,300	0.0033 - 0.087
Chromium	668 - 47,500	0.0066 - 0.47
Lead	3,100 - 100,000	< 0.016 - 7.3
Mercury	56[b]	0.0043
Nickel	230 - 49,000	< 0.004 - 0.57
Selenium	< 500 - 61,600	< 0.046 - 4.5
Silver	7.6 - 1,880	0.001 - 0.0064
Thallium	c	< 0.004 - 0.012

[a] ND - not detected in all runs.

[b] Detected during only one run; others not detected.

[c] Range could not be developed because of high < values.

of results focused on three areas: (a) QA/QC activities associated with the S&A program; (b) engineering evaluation of process monitoring data; and (c) analysis of data handling and reduction procedures, particularly those related to blank correction. These three areas are discussed in the paragraphs below.

4.3.1 Quality Assurance/Quality Control Results

The overall objective of the quality assurance activities associated with this program was to provide data of verifiable quality by making certain that: proper sampling and analysis methods were used; field sampling and laboratory equipment were adequately calibrated; standard field sampling and analysis protocols were followed; appropriate sample handling and transport procedures were followed; and chemical analyses were performed under controlled conditions. To realize this objective, QA/QC protocols were integrated into those tasks which impacted upon the sampling and analysis results. The QA/QC program for this study incorporated two primary aspects: (1) external quality assurance; and (2) internal quality assurance.

External quality assurance consisted of both system and performance audits of field and laboratory functions; the audits were conducted by an independent Quality Assurance Office. As part of the internal quality assurance program, standard operating procedures to assess and maintain quality of results were developed and followed by sampling and analysis personnel.

Significant program resources were committed to both internal and external quality assurance activities. Comprehensive external audits were conducted on the preparation for and conduct of sampling activities at three of the eight sites. Internal and external audits of laboratory analysis activities were conducted for samples from all eight sites. Throughout the program, external quality assurance activities involved determination of analytical accuracy for 751 volatile organic samples, 391 semivolatile organic samples, 21 chloride samples and 136 samples for 14 different metals. Internal laboratory audits for accuracy and precision involved the following numbers of samples:

Analyte Type	Precision	Accuracy
Volatile Organics	158	421
Semivolatile Organics	261	947
Metals	123	228

In most cases sufficient quality assurance data were obtained to verify the overall quality of the test data. The results of both the external and internal quality assurance programs indicate that established quality assurance protocols were followed and that the overall quality of the field and laboratory work was adequate to meet the objectives of this study. The external audit program results indicate that the overall performance and conduct of the field and laboratory work can be judged to be adequate. Results of the laboratory internal quality assurance program indicate that, overall:

- Analyses of volatile and semivolatile organic compounds were precise, generally within RSD ≦ 30% for replicate analyses.

- The level of accuracy (percent recovery) obtained during organic compound analysis was generally within expected ranges considering the complex sample matrices involved; the majority of the data were within the expected recovery range of 50 to 130%. This accuracy directly impacts the measured amounts of a compound in and out of an incinerator.

- Better accuracy (percent recovery) was obtained for volatile compounds than for semivolatile compounds.

- The fact that better percent recoveries for organic compounds were obtained for external audits than for actual samples is a strong indication that complex sample matrices do affect analytical results.

- Metals analyses were accurate and precise.

As expected for a program of this size, the analytical accuracy and/or precision obtained was less than desired for some specific cases. While these were often isolated cases, the quality assurance program results did identify some apparent systematic biases; e.g., consistently poor recoveries from all samples for a specific compound. Specific problems encountered which are discussed in more detail in Volume II include low or erratic recoveries during the analyses of phenol, cis- and trans-1,2-dichlorobutene, naphthalene, aniline, and bis(2-ethylhexyl)phthalate in complex matrices. This suggests caution when analyzing for these compounds.

4.3.2 Process Monitoring Data

The rate of oxidation of POHCs and associated incinerator performance are dependent on the time/temperature profile to which the POHCs are exposed and the availability of oxygen for reaction in the combustion chamber. Although actual reaction rates are dependent on microscale conditions within the incinerator, conditions are normally estimated based on overall combustion chamber temperature and residence time and stack gas O_2 concentration. The results from this program suggest that even the large scale parameters cannot be easily and consistently determined.

Specific problems encountered during this program included: (a) different chamber geometries and thermocouple locations from site to site make comparable estimates of combustion temperature difficult; and (b) both residence times and O_2 concentrations are based on stack gas measurements which might be biased by inleak air downstream from the combustion chamber. An engineering evaluation of the second problem using heat balance calculations was performed as a part of this program.

The values calculated from the heat balance suggest that inleak air may bias results for at least four of the eight facilities. For those four facilities the calculated stack gas flow rate ranged from 51 to 76% of the

measured flow rate. Further, the difficulties encountered during the engineering analysis illustrate the uncertainties regarding temperature and flow rate measurements from the eight sites. Because of these uncertainties, any conclusions regarding relationships between performance and incinerator operating parameters must be viewed with caution.

4.3.3 Data Handling and Reduction

In addition to the extensive sampling and analysis activities, the trial burn process involves a number of data handling and reduction activities. The evaluation of incinerator performance based on the DRE for specific POHCs has particularly intensive data reduction activities that normally involve several persons with different expertise. These activities range from calculation of POHC loadings in waste feed samples and sample traps by the analytical chemist based on mass spectrometer output, to the ultimate calculation of DRE by the scientist or engineer with a number of intermediate steps. The quality of the final result (determination of incinerator performance) is based on these intermediate activities.

One specific data reduction activity addressed during this study was blank correction for organic samples, particularly stack samples. Because incinerator stacks must contain extremely low concentrations of POHCs to achieve 99.99% DRE, contamination of stack samples can present problems. The problem of contamination is addressed by use of blank adsorbent traps and correction of sample values through the use of blank values. Since no standard procedure was available, a blank correction based on statistical analyses of both blank traps and sample traps was developed and used. However, additional research is needed to better define and validate a standard blank correction procedure to improve the quality and consistency of results from future trial burns.

4.4 SAMPLING AND ANALYSIS CONSIDERATIONS

Sampling and analysis procedures for hazardous waste incinerator emissions, and specifically trial burns for these incinerators, are still in a developmental stage. As a result, new procedures are being developed and old procedures modified on a continuing basis.

Although this program was not a methods development study, it did provide some insight into the evolving S&A procedures. This section discusses five of the more significant S&A issues encountered during the study: spiking problems, detection range concerns, volatile trap cleanup procedures, selection of analysis surrogates and comparison of gas bags and VOST for sampling volatile organics in stack gas. This list is not exhaustive; and the analyses presented are not comprehensive. Rather, the discussion provides examples of issues that need to be more fully addressed in developing and validating incinerator sampling and analysis protocols.

During trial burn type tests, spiking of specific POHCs into the waste feed may be used to assess the performance of the incinerator for selected waste feed characteristics. A 50/50 mixture of CCl_4 and TCE was continuously spiked into the waste feed line at five of the eight sites tested.

Analyses of samples collected downstream from the spiking point indicated that concentrations of CCl_4 and TCE were sometimes one-third to one-half the expected concentrations. Investigation of the problem indicated that poor mixing was the most likely cause. At the last plant, in-line mixers were installed prior to testing. Waste feed analyses for CCl_4 and TCE agreed closely with expected results at that site. These results suggest that in-line mixers may be needed whenever specific POHCs are spiked into the waste feed line.

Some difficulties were encountered in analyzing for volatile POHCs in stack gas samples when different specific POHCs were present in the stack gas at widely different concentrations. The method for analysis of volatile POHCs was designed to be able to quantify volatile POHCs so that a DRE of 99.99% is measurable at the 100 μg/g level of a POHC in the waste. The VOST method samples 20 L of stack effluent through each pair of traps. If the sample contained 1 ng/L of a POHC (as discussed above) the amount contained on any one pair of traps would be 20 ng, which is well above the detection limit of about 2 ng. However, analytical problems may arise when analyzing samples from incineration waste feeds with very wide range of concentration of POHCs. For example, if the concentration of a POHC in the waste were 100,000 μg/g (10%), the resulting POHC concentration in the stack effluent would be 1,000 ng/L if the incinerator was achieving a DRE of exactly 99.99%. In this case, the amount of POHC caught on any one pair of traps is 20,000 ng.

During thermal desorption, the entire collected sample enters the GC/MS and quantities as high as 20,000 ng could very likely saturate the MS detector. When this saturation of the primary characteristic ion occurs, as happened in a few cases in this program, the only alternative available is to perform the quantitation based on one of the minor fragmentation ions. When this technique is used, the results may not be as accurate as when the quantitation is based on the primary characteristic ion for the specific POHC.

Widespread problems with high blank for VOST traps during initial field testing suggested that the original cleanup procedures were not adequate. Extensive cleanup procedures were implemented to minimize problems. One of the key steps in the cleanup is purged heating of every trap, with FID analysis of the effluent purge as gas from each trap. No trap was considered clean and ready for shipment to the test site unless the FID analysis showed that the effluent purge gas contained less than 5 ppb of total hydrocarbons (based on propane as FID calibration gas). These procedures resulted in significantly reduced levels of blank trap contamination in later tests.

As a part of QA/QC activities, surrogate compounds were spiked into different types of samples (waste feeds, stack effluents, etc.) in order to better define the accuracy of the analytical methods. Results from this spiking showed variable recoveries for the surrogates in all types of samples. This variability made it difficult to use the surrogate analysis results in assessing the POHC results.

The most desirable surrogates would be the stable isotopically labeled forms of all, or at least some, of the POHCs of interest. However, the POHCs may not be known until after the waste has been analyzed. The cost and availability of the isotopically labeled compounds also may preclude their use. More investigative work is needed to facilitate appropriate selection of surrogates.

As a part of this study, two alternate methods for sampling volatile organics--gas bags and VOST--were compared. The comparison was made in three areas: (a) the relative level of incinerator performance (POHC concentration and DRE) as measured by each method; (b) the ability of each method to produce quantifiable emission rates (i.e., the ability to distinguish between sample values and blank values); and (c) the reliability and performance of the alternate methods based on judgments by sampling personnel. Differences in assessment of incinerator performance via the alternate methods are minimal, but VOST tends to produce more quantifiable results and have fewer operational problems. Based on the results of these tests, VOST appears to be more reliable than the gas bag method.

When both the gas bag and VOST results were quantifiable, the concentrations measured by the two methods did not differ significantly. The sampling method had a mixed effect on determination of DRE, but neither method showed inherent biases. Of the 88 cases during the eight tests where both gas bag and VOST had a DRE which was clearly on one side of 99.99%, the methods disagreed 19% of the time. Seven percent of the time the gas bag results indicated achievement of a DRE greater than 99.99% while the VOST did not. Twelve percent of the time the VOST results indicated achievement of a DRE a greater than 99.99% while the gas bag did not.

When the blank values for gas bags and VOST are converted to concentrations, the blank data clearly separate the first three tests from the last five. During the first three tests the concentration values for gas bag blanks were lower than those for VOST blanks 86% of the time. For the last five tests, the trend was reversed with concentration values for VOST blanks lower than those for gas bag blanks 93% of the time. The primary reason for this difference in values is that improved cleanup procedures for VOST traps evolved over the first three tests. The values for VOST blanks decreased by a factor of 35 or more for seven of the nine compounds when the average for the last five tests is compared to the average for the first three.

The improved VOST preparation procedures produced a very reliable set of data over the last five tests. Based on this data set, the VOST method produced only 19 observations which were indistinguishable from blank values (20% of the VOST observations). The gas bags produced 54 observations in which the sample was indistinguishable from the blank (57% of the gas bag observations).